Quantum Theory of the Solid State

Student Edition

JOSEPH CALLAWAY

Quantum Theory of the Solid State

Student Edition

To Mary

Preface

The purpose of this book is to describe the concepts and methods, and to introduce some of the central problems of the quantum theory of solids. It should be suitable as a textbook for students who have completed a one-year course in quantum mechanics and have some familiarity with the experimental facts of solid state physics. It should also be useful as a reference work. I have attempted a moderately comprehensive coverage: The physics of solids is, in fact, a rather diverse subject.

A book with these aims must develop both principles and mathematical techniques; in addition, it should assist the reader in making his way through the more specialized periodical literature. To this end, fairly lengthy bibliographies have been included at the end of each chapter, although these are not intended to be complete in any area. If these references are used in conjunction with the Science Citation Index, it should be possible to follow many specific subjects to the frontier of present research.

This work is intended to be a single intellectual unit, although for reasons of convenience it has been divided into two parts. Part A contains much of the formalism required for the theoretical study of solids; Part B is oriented toward more specific problems. Thus, Part A includes phenomenological treatments of lattice vibrations and magnetic order, a discussion of symmetry groups, and a description of the properties of one-electron wave functions and the principal techniques for calculating energy levels. In Part B the machinery developed previously is applied to impurities, disordered systems, the effects of external fields, and transport phenomena (including superconductivity). The book concludes with an introduction to many-body theory, including some applications.

The specific selection of topics is obviously a personal one, and some areas of considerable importance, such as mechanical properties, surfaces, electron diffraction, and amorphous materials, have not been included. Experimental results are used occasionally and illustratively. There is no

detailed confrontation of specific approximations with experimental data. MKS, cgs, and atomic units have been used rather interchangeably. Some problems have been included.

I am indebted to my colleague, Dr. John Kimball, and to several students (W. Y. Ching, M. Eswaran, G. S. Grest, W. Y. Hsia, M. Singh, and C. S. Wang) for critical readings of portions of the manuscript.

Note to the Reader

In Part B the superscript "plus" ($+$) is used to indicate a Hermitian adjoint instead of the superscript "dagger" ($\dagger$) used in Part A.

Contents

v

Chapter 4.   Energy Bands

APPENDICES TO PART A

PART B

Chapter 5.   Impurities and Alloys

Chapter 6. **External Fields**

Chapter 7. **Electrons and Phonons**

Chapter 8. **Aspects of the Electron–Electron Interaction**

CHAPTER 1

Lattice Dynamics

In this chapter we will present some portions of the theory of the vibrations of crystal lattices. We will also describe some of the geometrical relations and constructions which are useful in almost all branches of the theory of solids. Our point of view with respect to the lattice vibrations will be phenomenological, that is, we will assume that the forces between atoms are known and can be described by a set of force constants, which are the second derivatives of the interatomic potentials with respect to atomic displacements. The displacements themselves are assumed to be small, so that for the most part, the forces may be regarded as linear functions of the atomic displacements. This is the harmonic approximation; the lattice is treated as a collection of coupled simple harmonic oscillators. It is the task of a more fundamental theory to determine the interatomic potential and thus the force constants which we have regarded as disposable parameters, apart from general restrictions imposed by symmetry and invariance considerations.

1.1 Equations of Motion and Their Solution

In this section we will obtain the general equations of motion for a vibrating lattice and indicate the method of solution with respect to a simple example. The treatment is largely based on the presentation of Maradudin *et al.* (1971).

1.1.1 *The Dynamical Matrix*

The periodicity of a crystal is described by a set of vectors $\mathbf{R}_i$ which locate each unit cell in the crystal. We assume the crystal contains a large

or even an infinite number of unit cells and neglect any effects due to boundary surfaces. Each $\mathbf{R}_i$ may be expressed in terms of three independent (noncoplanar) primitive translation vectors ($\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$) in the following way:

$$\mathbf{R}_i = n_{i1}\mathbf{a}_1 + n_{i2}\mathbf{a}_2 + n_{i3}\mathbf{a}_3 \qquad (1.1.1)$$

where the n_{ij} are integers. Each unit cell contains r atoms. The locations of the r atoms are given by the vectors $\mathbf{d}_\kappa$ where κ indicates the different atoms in the unit cell, and takes the values 1, 2, $\ldots$, r. The general position of the κth atom in the ith unit cell is then

$$\mathbf{X}_{i\kappa} = \mathbf{R}_i + \mathbf{d}_\kappa. \qquad (1.1.2)$$

We now suppose that each atom is displaced from its equilibrium position by an amount $\mathbf{u}_{i\kappa}$ (the αth rectangular component of $\mathbf{u}_{i\kappa}$ is denoted by $u_{\alpha,i\kappa}$). The mass of the κth atom is M_κ. The atoms are heavy enough so that their behavior can, in most instances, be described classically.

The total kinetic energy of the lattice is therefore

$$T = \tfrac{1}{2} \sum_{\alpha,\,i,\,\kappa} M_\kappa \dot{u}^2_{\alpha,\,i\kappa} \qquad (1.1.3)$$

where the dot indicates derivative with respect to time.

Let the total potential energy of the crystal be denoted by Φ. This quantity will be a function of the atomic positions. When the atoms are displaced from their equilibrium positions, Φ will differ from its equilibrium value Φ_0. This difference may be expressed as a Taylor series in the atomic displacements

$$\Phi = \Phi_0 + \sum_{i\kappa\alpha} \Phi_{\alpha,\,i\kappa} u_{\alpha,\,i\kappa} + \tfrac{1}{2} \sum_{i\kappa\alpha,\,j\nu\beta} \Phi_{\alpha\beta,\,i\kappa,\,j\nu} u_{\alpha,\,i\kappa} u_{\beta,\,j\nu} + \cdots. \qquad (1.1.4)$$

In this chapter we will make the harmonic approximation, that is, we will neglect terms in (1.1.4) higher than second order in the atomic displacements. The quantities Φ_α are derivatives of the potential energy.

$$\Phi_{\alpha,\,i\kappa} = [\partial\Phi/\partial u_{\alpha,\,i\kappa}]_0, \qquad \Phi_{\alpha\beta,\,i\kappa,\,j\nu} = [\partial^2\Phi/\partial u_{\alpha,\,i\kappa}\,\partial u_{\beta,\,j\nu}]_0. \qquad (1.1.5)$$

The subscript 0 indicates that the derivatives are evaluated in the equilibrium configuration of the crystal.

It is apparent that $\Phi_{\alpha,\,i\kappa}$ in the negative of the αth component of the net force on atom $i\kappa$ in its equilibrium position. However, this notion is contredictory in that if there were a net force on an atom, it would move, and so the original position would not have been one of equilibrium. Thus we must have

$$\Phi_{\alpha,\,i\kappa} = 0. \qquad (1.1.6)$$

The Hamiltonian of the system is therefore

$$H = \Phi_0 + \tfrac{1}{2} \sum M_\kappa \dot{u}^2{}_{\alpha,i\kappa} + \tfrac{1}{2} \sum_{\alpha i\kappa, \beta j\nu} \Phi_{\alpha\beta, i\kappa, j\nu} u_{\alpha,i\kappa} u_{\beta, j\nu}. \qquad (1.1.7)$$

The equations of motion of the lattice are then easily found to be

$$M_\kappa \ddot{u}_{\alpha, i\kappa} = -\partial\Phi/\partial u_{\alpha, i\kappa} = -\sum_{\beta j\nu} \Phi_{\alpha\beta, i\kappa, j\nu} u_{\beta, j\nu}. \qquad (1.1.8)$$

There are a number of restrictions that may be imposed by general physical considerations on the coefficients $\Phi_{\alpha\beta, i\kappa, j\nu}$. Some of these include:

(1) $\Phi_{\alpha\beta, i\kappa, j\nu}$ depends on $\mathbf{R}_i$ and $\mathbf{R}_j$ only through their vector difference $\mathbf{R}_i - \mathbf{R}_j$. This follows because we may displace the origin of coordinates arbitrarily without altering the $\Phi_{\alpha\beta}$.

(2) Suppose the lattice is displaced rigidly (all $u_{\beta, j\nu}$ are made independent of j and ν). No acceleration can result. Thus

$$\sum_{j\nu} \Phi_{\alpha\beta, i\kappa, j\nu} = 0. \qquad (1.1.9)$$

Other restrictions are derived by Maradudin *et al.* (1971).

Let us obtain periodic solutions to (1.1.8). We write

$$u_{\alpha, i\kappa} = M_\kappa{}^{-1/2} u_{\alpha, \kappa}(\mathbf{k}) \exp[-i\omega t + i\mathbf{k}\cdot\mathbf{R}_i]. \qquad (1.1.10)$$

Here $u_{\alpha, \kappa}(\mathbf{k})$ is assumed to be independent of $\mathbf{R}_i$. This is to be substituted into (1.1.8). We obtain

$$-M_\kappa{}^{1/2}\omega^2 \exp[-i\omega t + i\mathbf{k}\cdot\mathbf{R}_i] u_{\alpha, \kappa}(\mathbf{k})$$
$$= -\sum_{\beta j\nu} M_\nu{}^{-1/2} \Phi_{\alpha\beta, i\kappa, j\nu} u_{\beta, \nu}(\mathbf{k}) \exp[-i\omega t + i\mathbf{k}\cdot\mathbf{R}_i + i\mathbf{k}\cdot(\mathbf{R}_j - \mathbf{R}_i)].$$

$$(1.1.11)$$

Since Φ depends only on $\mathbf{R}_i - \mathbf{R}_j$, we may replace the sum over $\mathbf{R}_j$ by one on $\mathbf{R}_i - \mathbf{R}_j$. Thus we have the set of simultaneous equations

$$\omega^2 u_{\alpha, \kappa}(\mathbf{k}) = \sum_{\nu\beta} D_{\alpha\beta, \kappa\nu}(\mathbf{k}) u_{\beta, \nu}(\mathbf{k}) \qquad (1.1.12)$$

where

$$D_{\alpha\beta, \kappa\nu}(\mathbf{k}) = (M_\kappa M_\nu)^{-1/2} \sum_{\mathbf{R}_i - \mathbf{R}_j} \Phi_{\alpha\beta, i\kappa, j\nu} \exp[-i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{R}_j)]. \qquad (1.1.13)$$

D is frequently referred to as the "dynamical matrix," and $\mathbf{k}$ is the wave vector of the vibrational wave. The condition for the set of linear homogeneous equations to possess a nontrivial solution is

$$\det[\omega^2 \delta_{\alpha\beta} \delta_{\kappa\nu} - D_{\alpha\beta, \kappa\nu}(\mathbf{k})] = 0. \qquad (1.1.14)$$

The matrix D is of dimension $3r \times 3r$ (recall that r is the number of atoms in the unit cell). Furthermore, it is Hermitian:

$$D^*{}_{\beta\alpha,\nu\kappa}(\mathbf{k}) = \sum_{\mathbf{R}_i - \mathbf{R}_j} \Phi_{\beta\alpha,i\nu,j\kappa} \exp[-i\mathbf{k}\cdot(\mathbf{R}_j - \mathbf{R}_i)]$$

$$= \sum \Phi_{\alpha\beta,j\kappa,i\nu} \exp[-i\mathbf{k}\cdot(\mathbf{R}_j - \mathbf{R}_i)] = D_{\alpha\beta,\kappa\nu}(\mathbf{k}). \quad (1.1.15)$$

We have used the symmetry property of the derivatives of Φ that $\Phi_{\beta\alpha,i\nu,j\kappa} = \Phi_{\alpha\beta,j\kappa,i\nu}$.

Thus we see that there are $3r$ real eigenvalues to be determined. We denote these eigenvalues by $\omega_j{}^2(\mathbf{k})$ ($j = 1, \ldots, r$). They are the squares of the normal mode frequencies for the crystal. The index j designates a branch; and within a branch ω^2 will be a continuous function of $\mathbf{k}$ (out to a certain limit, as we will find later).

The equation

$$\omega = \omega_j(\mathbf{k}) \qquad (j = 1, 2, \ldots, 3r) \quad (1.1.16)$$

is known as the *dispersion relation* for the crystal.

For each of the $3r$ values of ω for given $\mathbf{k}$, there is an eigenvector of D which we denote by $\mathbf{e}^{(j)}$, or $e_{\alpha,\nu}{}^{(j)}(\mathbf{k})$. This satisfies

$$\omega_j{}^2(\mathbf{k})e_{\alpha,\nu}{}^{(j)}(\mathbf{k}) = \sum_{\beta\kappa} D_{\alpha\beta,\nu\kappa}(\mathbf{k})e_{\beta,\kappa}{}^{(j)}(\mathbf{k}). \quad (1.1.17)$$

These vectors are determined by (1.1.17) only up to a constant factor; however, they may be normalized conveniently. The e's are in fact elements of a unitary matrix which diagonalizes D. As a result, we have both orthonormality and completeness relations in the form

$$\text{orthonormality:} \quad \sum_{\alpha,\kappa} e_{\alpha,\kappa}{}^{(j)*}(\mathbf{k})e_{\alpha,\kappa}{}^{(i)}(\mathbf{k}) = \delta_{ji}, \quad (1.1.18a)$$

$$\text{completeness:} \quad \sum_{j} e_{\alpha,\kappa}{}^{(j)*}(\mathbf{k})e_{\beta,\nu}{}^{(j)}(\mathbf{k}) = \delta_{\alpha\beta}\,\delta_{\kappa\nu}. \quad (1.1.18b)$$

Since the $\Phi_{\alpha\beta}$ are real, it follows from (1.1.13) that

$$D_{\alpha\beta,\kappa\nu}(-\mathbf{k}) = D^*{}_{\alpha\beta,\kappa\nu}(\mathbf{k}). \quad (1.1.19)$$

Since D is Hermitian, the eigenvalues are always real; it therefore follows that

$$\omega_j{}^2(\mathbf{k}) = \omega_j{}^2(-\mathbf{k}). \quad (1.1.20)$$

This relation can also be shown to be a consequence of time reversal symmetry.

If we now take the complex conjugate of Eq. (1.1.17), we see that the eigenvectors must be proportional:

$$e_{\alpha,\kappa}{}^{(j)*}(\mathbf{k}) = ce_{\alpha,\kappa}{}^{(j)}(-\mathbf{k}).$$

We require that completeness and orthonormality relations hold for $(-\mathbf{k})$ as well as for $(\mathbf{k})$ so that c must be a complex number of modulus unity. We will choose c to be 1, so that

$$e_{\alpha,\kappa}{}^{(j)*}(\mathbf{k}) = e_{\alpha,\kappa}{}^{(j)}(-\mathbf{k}). \tag{1.1.21}$$

1.1.2 Some Properties of the Vibrational Spectrum

Three of the branches of the spectrum are such that ω goes to 0 as $\mathbf{k}$ goes to 0. To see this, set $\mathbf{k} = 0$ in (1.1.17), which then becomes

$$\omega_j{}^2(0)e_{\alpha\kappa}{}^{(j)}(0) = \sum_{\beta j\nu} \left[\Phi_{\alpha\beta,\,i\kappa,j\nu}/(M_\kappa M_\nu)^{1/2} \right] e_{\beta\nu}{}^{(j)}(0). \tag{1.1.22}$$

Now we can solve (1.1.22) trivially by supposing that, for each β, $(e_{\beta\nu}(0)/M_\nu{}^{1/2})$ is independent of ν. Then the right side of (1.1.22) vanishes because of (1.1.9) and we have a solution with $\omega = 0$.

The modes which have this property are called *acoustic modes*. The remaining $3r - 3$ modes are called *optical modes*. The atomic displacements corresponding to the $\omega = 0$ acoustic modes are, from (1.1.10)

$$\mathbf{u}_{i\kappa} = M_\kappa{}^{-1/2}\mathbf{e}_\kappa(0) = \text{const.}$$

All r particles in each unit cell move in parallel with equal amplitudes. This is characteristic of an elastic wave of infinite wavelength.

Let us now consider the case of $r = 2$, corresponding to an ionic crystal with two atoms in each unit cell. We apply Eq. (1.1.18a) and let j refer to one of the optical branches while i refers to any of the acoustic branches. Further, we allow κ to take the values $+, -$ which may be considered to refer to the ions of positive and negative charge, respectively. We may now write Eq. (1.1.18a)

$$\mathbf{e}_+{}^{(j)}(0) \cdot \mathbf{e}_+{}^{(i)}(0) + \mathbf{e}_-{}^{(j)}(0) \cdot \mathbf{e}_-{}^{(i)}(0) = 0. \tag{1.1.23}$$

We have already seen that for the acoustic branch

$$\mathbf{e}_+{}^{(i)}(0)/M_+{}^{1/2} = \mathbf{e}_-{}^{(i)}(0)/M_-{}^{1/2}.$$

Thus we have

$$\mathbf{e}_+{}^{(i)}(0) \cdot \left[\mathbf{e}_+{}^{(j)}(0) + (M_-/M_+)^{1/2}\mathbf{e}_-{}^{(j)}(0) \right] = 0.$$

Since the three polarization vectors $\mathbf{e}^{(i)}$ ($i = 1, 2, 3$) for the acoustic modes are independent, it follows that

$$M_+{}^{1/2}\mathbf{e}_+{}^{(j)}(0) + M_-{}^{1/2}\mathbf{e}_-{}^{(j)}(0) = 0 \tag{1.1.24}$$

which implies, through (1.1.10), that

$$M_+\mathbf{u}_{i+} + M_-\mathbf{u}_{i-} = 0. \tag{1.1.25}$$

This result may be interpreted as meaning that the two ions in any unit cell vibrate 180° out of phase with each other, but in such a way that the center of mass of the cell remains fixed. Because the two ions have opposite charges, there will be a net oscillating dipole moment in the crystal. Recall that from (1.1.10), since we are concerned with $k = 0$, each cell will vibrate in phase with every other cell. Such a dipole moment can interact with an external electric field, and this gives the modes their name. In the case of more than two atoms per unit cell, the interpretation will not be so simple.

We continue with the case $r = 2$, and now consider a cubic crystal. We will determine the frequency of the vibrations at $k = 0$. We multiply (1.1.17) by $e_{\alpha\nu}^{(j)*}(\mathbf{k})$ and sum over $\alpha\nu$. With the use of (1.1.18a) we have

$$\omega_j^2(\mathbf{k}) = \sum_{\alpha\nu, \beta\kappa} e_{\alpha,\nu}^{(j)*}(\mathbf{k}) D_{\alpha\beta,\nu\kappa}(\mathbf{k}) e_{\beta,\kappa}^{(j)}(\mathbf{k}). \qquad (1.1.26)$$

This is very much like a quantum mechanical expectation value, and is valid for any $\mathbf{k}$. Now we substitute for D, using (1.1.12), and put $k = 0$ explicitly:

$$\omega_j^2(0) = \sum_{\alpha\nu, \beta\kappa, R_i-R_l} (M_\kappa M_\nu)^{-1/2} e_{\alpha,\nu}^{(j)*}(0) \, \Phi_{\alpha\beta, i\nu, l\kappa} e_{\beta,\kappa}^{(j)}(0). \qquad (1.1.27)$$

We now manipulate this expression. Write out the sum over ν and κ explicitly in terms of $+$ and $-$:

$$\omega_j^2(0) = \sum_{\alpha\beta, R_i-R_l} \{ e_{\alpha+}^{(j)*}(0) [(M_+)^{-1} \Phi_{\alpha\beta, i+, l+} e_{\beta+}^{(j)}(0)$$
$$+ (M_+ M_-)^{-1/2} \Phi_{\alpha\beta, i+, l-} e_{\beta-}^{(j)}(0)]$$
$$+ e_{\alpha-}^{(j)*}(0) [(M_+ M_-)^{-1/2} \Phi_{\alpha\beta, i-, l+} e_{\beta+}^{(j)}(0)$$
$$+ (M_-)^{-1} \Phi_{\alpha\beta, i-, l-} e_{\beta-}^{(j)}(0)] \}.$$

Then we use (1.1.24) and (1.1.9) to obtain

$$\omega_j^2(0) = \sum_{\alpha\beta, R_i-R_l} \{ [e_{\alpha+}^{(j)*}(0) e_{\beta+}^{(j)}(0) + e_{\alpha-}^{(j)*} e_{\beta-}^{(j)}(0)]$$
$$\times [(\Phi_{\alpha\beta, i+, l+}/M_+) + (\Phi_{\alpha\beta, i-, l-}/M_-)] \}. \qquad (1.1.28)$$

We now assume the crystal is cubic. In this case, if we sum over all lattice sites, terms with $\alpha \neq \beta$ must disappear, since transformations such as $x \to x, \, y \to -y, \, z \to z$ change the sign of the second derivatives but cannot change the potential energy of the system. Similarly, the application of transformations such as $x \to y, \, y \to x, \, z \to z$ shows that all diagonal ($\alpha = \beta$) terms are equal. Thus

$$\sum_{R_i-R_l} \Phi_{\alpha\beta, i\pm, l\pm} = \delta_{\alpha\beta} \sum_{R_i-R_l} \Phi_{\alpha\alpha, i\pm, l\pm}, \qquad (1.1.29)$$

and the right side is independent of α. We can use this result in combination with (1.1.18a) to obtain

$$\omega_j{}^2(0) = \sum_{R_i - R_l} [(\Phi_{\alpha\alpha, i+, l+}/M_+) + (\Phi_{\alpha\alpha, i-, l-}/M_-)]. \quad (1.1.30)$$

The right side of (1.1.30) is independent of j, and we may therefore conclude that the frequencies of all three optical modes at $k = 0$ in a cubic crystal are equal.

We now want to consider the small k behavior of the acoustic branches in more detail. In this case, ω becomes linearly proportional to k, the proportionality constant being the appropriate velocity of sound. As the algebra can, in the general case, become quite messy we consider here only a monatomic lattice (one atom per unit cell). In this case, we may drop the indices κ and ν, and consider Eq. (1.1.11) in the form

$$\omega^2(\mathbf{k})u_\alpha(\mathbf{k}) = \sum_\beta D_{\alpha\beta}(\mathbf{k})u_\beta(\mathbf{k}). \quad (1.1.31)$$

We expand the dynamical matrix in powers of $\mathbf{k}$, since $\mathbf{k}$ is considered to be small. Thus

$$D_{\alpha\beta}(\mathbf{k}) = D_{\alpha\beta}(0) + \sum_\gamma c_{\alpha\beta,\gamma}k_\gamma + \sum_{\gamma\delta} c_{\alpha\beta,\gamma\delta}k_\gamma k_\delta + \cdots \quad (1.1.32)$$

where

$$D_{\alpha\beta}(0) = (1/M) \sum_{R_i - R_j} \Phi_{\alpha\beta}(\mathbf{R}_i - \mathbf{R}_j) = (1/M) \sum_i \Phi_{\alpha\beta}(\mathbf{R}_i); \quad (1.1.33)$$

also

$$c_{\alpha\beta,\gamma} = (1/M) \sum_i \Phi_{\alpha\beta}(\mathbf{R}_i)x_\gamma{}^{(i)}, \quad (1.1.34)$$

$$c_{\alpha\beta,\gamma\delta} = (-1/2M) \sum_i \Phi_{\alpha\beta}(\mathbf{R}_i)x_\gamma{}^{(i)}x_\delta{}^{(i)}. \quad (1.1.35)$$

We have defined $x_\gamma{}^{(i)} = (\mathbf{R}_i)_\gamma$. It is possible, however, to show that $c_{\alpha\beta,\gamma}$ vanishes. This may be seen if we realize that the second derivatives of the potential energy must be even functions of $\mathbf{R}_i - \mathbf{R}_j$. This follows since the atomic interactions must be assumed to be unchanged by an inversion, that is, if $\mathbf{R}_i \rightarrow -\mathbf{R}_i$ and $\mathbf{R}_j \rightarrow -\mathbf{R}_j$. Then, there will be compensatory contributions from $\mathbf{R}_i$ and $-\mathbf{R}_i$. Also, we have from (1.1.9) that $D_{\alpha\beta}(0) = 0$. [This leads to $\omega^2(0) = 0$ in this case.] Hence our small k formula is

$$\omega^2(\mathbf{k})u_\alpha(\mathbf{k}) = \sum_{\nu\delta\beta} [c_{\alpha\beta,\nu\delta}k_\nu k_\delta]u_\beta(\mathbf{k}). \quad (1.1.36)$$

The frequency ω can be expanded as a power series in the components of $\mathbf{k}$.

Since $\omega_j(0) = 0$, the leading term in this is of order k, and, therefore, the leading dependence of ω^2 on the magnitude of $\mathbf{k}$ is of second order. This being so, we may neglect the dependence of u_α on $|\mathbf{k}|$. It will, however, continue to depend on direction so we will denote it by $u_\alpha(\hat{\mathbf{k}})$. Thus we have

$$\omega^2 u_\alpha(\hat{\mathbf{k}}) = \sum_{\nu\delta\beta} c_{\alpha\beta,\nu\delta} k_\nu k_\delta u_\beta(\hat{\mathbf{k}}). \qquad (1.1.37)$$

This equation has the same form as the equation determining the vibration frequencies for an elastic continuum. We must consider (1.1.37) as an eigenvalue equation. This equation determines the proportionality constant between ω and $|\mathbf{k}|$ for the three possible acoustic waves. This proportionality constant is the relevant sound velocity. The direction cosines of the polarization vectors are also determined.

1.1.3 *Example*: *A Simple Cubic Lattice*

Let us illustrate these considerations by discussing a relatively simple case: a monatomic, simple cubic lattice of lattice constant a in which forces are assumed to act between one atom and its first and second nearest neighbors. The forces are assumed to be central, that is, the potential energy is a function of the distance between atomic pairs only (and not angle). Only those displacements which change the distance between atoms (in first order) will contribute to Φ. Such displacements must be along the vector connecting the atoms in equilibrium. Let $\mathbf{u}_i$ be the displacement vector for atom i. We have the potential function

$$\Phi = \Phi_0 + (\alpha/2a^2) \sum_{ij,\,\text{nn}} [(\mathbf{R}_i - \mathbf{R}_j) \cdot (\mathbf{u}_i - \mathbf{u}_j)]^2$$
$$+ (\gamma/2a^2) \sum_{ij,\,\text{sn}} [(\mathbf{R}_i - \mathbf{R}_j) \cdot (\mathbf{u}_i - \mathbf{u}_j)]^2 \qquad (1.1.38)$$

where nn indicates nearest neighbors, sn second neighbors, and the constants α and γ are second derivatives of the potential energy. Let a be the lattice constant, and x_i be the x component of u_i with respect to the crystal axes, etc. Then

$$\alpha = -(\partial^2\Phi/\partial x_i \partial x_j) \qquad \text{for} \quad |\mathbf{R}_i - \mathbf{R}_j| = a, \qquad (1.1.39)$$

$$\gamma = -(\partial^2\Phi/\partial x_i \partial x_j) \qquad \text{for} \quad |\mathbf{R}_i - \mathbf{R}_j| = 2^{1/2}a. \qquad (1.1.40)$$

The sum in (1.1.38) includes different nearest neighbor pairs. In order to make the notation more transparent in the following, we replace the single